Dissolved organic matter in shelf waters off the Ría de Vigo (NW Iberian upwelling system)

X.A. Álvarez-Salgado*, M.D. Doval, F.F. Pérez

Instituto de Investigacións Mariñas (CSIC)

Eduardo Cabello 6, 36208-Vigo, Spain

*author to whom correspondence should be addressed:

Tel: +34 86 29 86 13

Fax: +34 86 29 27 62

email: xsalgado@iim.csic.es

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Abstract

Net in situ production and export of dissolved organic carbon (DOC) and nitrogen (DON) have been studied in shelf waters off the Ría de Vigo (NW Spain), as part of a comprehensive hydrographic survey carried out from September 1994 to September 1995 with a fortnight periodicity. DOC and DON correlated well (r = +0.78), the slope of the regression line being 12.0±0.7 mol-C·mol-N^{-1}, about twice the Redfieldian slope of particulate organic matter, 6.5±0.2 mol-C·mol-N^{-1} (r = +0.95). Labile DOC and DON accumulated in the upper 50m during the upwelling season (March-September), mainly after prolonged periods of wind relaxation, when horizontal flows were reduced. This labile material represented 50% and 35% of the total (dissolved+particulate) organic carbon and nitrogen susceptible of microbial utilisation, which assert the key contribution of dissolved organic matter (DOM) to the export of new primary production in the NW Iberian upwelling system. This surface excess in shelf waters appeared to be formed into the highly productive Ría de Vigo (a large coastal indentation) at net rates of ~4.4 µM-C·d^{-1} and ~1.3 µM-C·d^{-1} in the inner and outer segments of the embayment respectively, and subsequently exported to the shelf. Once in the shelf, simple dilution with the inert DOM pool of recently upwelled Eastern North Atlantic Central Water (ENACW) occurred. Eventually, the DOM excess produced during the upwelling season is exported to the adjacent open ocean waters by the coastal circulation. Conversely, during the unproductive downwelling season (October-February), the lowest DOC and DON levels were recorded and export was prevented by the characteristic downwelling front associated to the seasonal poleward slope current.

Keywords: DOC, DON, upwelling, downwelling, NW Iberian Peninsula

1. Introduction

The efficiency in the transference of organic material produced in coastal areas to the adjacent ocean has been a subject of active discussion for marine biogeochemists over the last 15 years (Walsh et al., 1981; Walsh et al., 1988; Wroblewski and Hoffmann, 1989; Biscaye et al., 1994; Pilskaln et al., 1996). However, the contrasting hypothesis of export to the deep ocean *versus* oxidation on the shelf have only considered the fate of particulate organic matter (POM) (Hansell et al., 1993). Recent studies in ocean areas where convective mixing occurs have confirmed the major contribution of biologically-produced labile dissolved organic matter (DOM) to the annual downward flux of organic material (Copin-Montégut and Avril, 1993; Carlson et al., 1994; Lefèvre et al., 1996; Børsheim and Myklestad, 1997). Conversely, the contribution of horizontal transport to the export (~new) production in areas where horizontal fluxes are important has been assessed in the Equatorial Pacific, with controversial results: Peltzer and Hayward (1996) show that horizontal export of DOM is the fate of 50-75% of the carbon fixed by new primary production, whereas Hansell et al. (1997) estimated a contribution of <6%. Horizontal fluxes intensified in ocean margins, specially where wind-driven upwelling occurs (Wroblewski and Hoffmann, 1989; Gabric et al., 1993). In addition, fuelling of biogeochemical processes (Mantoura et al., 1991; Walsh, 1991; Wollast, 1993) must enhance the production of labile DOM. Consequently, the contribution of this new pool needs to be considered in any realistic biogechemical model of carbon and nitrogen in ocean margins.

The northwestern coast of the Iberian Peninsula (42º-43º N) is affected by the intermittent (period, 10-15 d) wind-driven upwelling of nutrient-rich Eastern North Atlantic Central Water (ENACW) from *ca*. April to September (Blanton et al., 1987;

Álvarez-Salgado et al., 1993; Rosón et al., 1997). Large filaments are observed along the Iberian coast (Haynes et al., 1993). Form *ca*. October to March, southerly winds prevailed and a downwelling front develops in the slope, precluding shelf-edge exchange (Castro et al., 1997). A strong poleward flow of subtropical ENACW happens along the slope (Haynes and Barton, 1990; 1991), which has been observed as south as Cape San Vicente (Ambar et al., 1984; Frouin et al., 1990) and penetrates as north as the Armorican shelf (Pingree and Le Cann, 1990). Intense nutrient enrichment by organic matter mineralization occurs in shelf bottom waters of the NW Iberian upwelling system over year (Prego and Bao, 1997; Álvarez-Salgado et al., 1997). Four large coastal embayments in the survey area (the Rías Baixas), where the upwelled nutrients are efficiently trapped (Prego, 1993; Álvarez-Salgado, 1996a), have some impact on nutrient cycling in shelf waters (Fraga, 1981; Álvarez-Salgado et al., 1993; 1997; Prego, 1994).

Although nutrients have been recurrently mapped, a lack of information exists regarding POM and DOM in shelf waters off the Rías Baixas. Particulate and dissolved organic carbon and nitrogen pools were measured as part of a joint effort of the 'Instituto de Investigacións Mariñas' (CSIC) and the 'Instituto Español de Oceanografia' to study the wind-driven seasonal hydrographic variability in shelf waters off the Ría the Vigo. The present contribution, dealing with the distribution, characterisation, origin and fate of DOM, is complementary to the recent work by Doval et al. (1997a) describing the thermohaline and nutrient variability.

2. Materials and methods

A 3-station radial transect was surveyed with a fortnight periodicity from September 1994 to September 1995, starting at the time series station (stn 15; 42°14.5'N, 8°45.8'W) on the main channel of the Ría de Vigo (water depth, 45m) and ending at stn 11 (42°07.8'N, 9°07.5'W) in the middle of the shelf (water dept, 140m), about 35 Km offshore (Fig. 1). The outermost station was only surveyed during the upwelling season, because bad weather conditions during the winter prevented us to arrive there with our 15m long inshore boat. Therefore, we will mainly refer to stn 13 (42°08.5'N, 8°57.5'W; water depth, 90m), although we have also some gaps by January-February and by April-May.

A Seabird Electronics 25-01 CTD was dipped before the bottle cast. Then, seawater samples were taken with 5-l Niskin bottles from fixed depths: 0, 15 and 40m at stn 15; 5, 20, 30, 40, 50, 70 and 85m at stn 13; and 5, 20, 30, 50, 70, 100 and 130m at stn 11. Analyses of O_2, 5-nutrients, pH (NBS), alkalinity, fluorometric chlorophyll-*a* (chl-*a*), POC, PON, DOC and DON were performed at the IIM base laboratory in Vigo (see Doval et al., 1997a).

Chl-*a* was determined with a Turner Designs 10000R fluorometer, after 90% acetone extraction (Yentsch and Menzel, 1963). A volume of 1 l of sample was filtered through an oilless vacuum filtration system. Particulate organic carbon (POC) and nitrogen (PON) were collected on Whatman GF/F filters, which were dried and frozen to -20ºC until analysis. Measurements were carried out with a Perkin Elmer 2400 CHN analyser. Aliquots of the filtrate were taken for DOC and DON analyses. DOC determination was performed by high temperature catalytic oxidation (HTCO) with a commercial Shimadzu TOC-5000 (Doval et al., 1997b). The combustion quartz tube was filled with a 0.5% Pt on Al_2O_3 catalyst. Three to 5 replicate injections of 200 µl were performed per sample. The concentration of DOC was determined by subtracting the average peak area from the instrument blank area and dividing by the slope of the standard curve (Thomas et al., 1995). The instrument blank is the system blank plus the filtration blank. DOC-free UV irradiated Milli-Q water (<2 µM-C) was injected to quantify the system blank (8 µM-C). The filtration blank (5 µM-C) was determined with UV-Milli-Q water previously run through the filtration device. The coefficient of variation (C.V.) of the peak area for the 3-5 replicates of each sample was ~1%. DON was measured by the Kjeldahl method, after removal of inorganic nitrogen salts (Doval et al., 1997c). A volume of 100 ml of sample was introduced into a 300 ml Pyrex Kjeldahl flask. To eliminate ammonium, 1 ml of 0.5 N NaOH was added and the solution was boiled until sample was reduced by a half. Next, 10 ml of H_2SO_4-$FeSO_4$ reagent were added to remove nitrogen oxides. The heating must go on to convert DON to ammonium in acid medium. The residue was diluted with UV-Milli-Q water and carried to a distillation device, where 20 ml of 33% NaOH were added. Ammonia was co-distilled with water vapour until 20 ml were collected over 5 ml of 10^{-3} M HCl. Ammonium concentration on the distillate, directly relate to DON in the sample, was finally determined with a Technicon AAII system. The average blank was 2 µM-N. We analysed duplicate seawater samples, being the C.V. 5 %.

The upwelling index (I_W), an estimation of the flow of upwelled water per kilometre of coast, was calculated following Wooster et al. (1976):

$$I_W = \frac{\rho_a \cdot C \cdot |\vec{V}|}{f \cdot \rho_W} V_{II}$$

where ρ_a is the density of air, 1.2 kg m^{-3} at 15 ºC; C is an empirical drag coefficient (dimensionless), $1.3 \cdot 10^{-3}$; f is the Coriolis parameter, $9.9 \cdot 10^{-5}$ s^{-1} at 43º latitude; ρ_w is the density of seawater, 1025 kg m^{-3}; $|\vec{V}|$ is wind speed and V_{II} is the component of wind speed parallel to the coast, as the coastline is rotated ~15° regarding the N—S direction (see the 100m depth line in Fig. 1). Daily averaged geostrophic winds at 43°N 11°W (stn G1), deduced from surface pressure charts were used (Bakun, 1973). $\langle I_W \rangle$ is the average I_W from the current day to 2 days before (Rosón et al., 1997). Negative values indicate downwelling.

3. Results and discussion

3.1. *Hydrographic setting*

The characteristic wind-featured seasons in the NW Iberian upwelling system can be easily identified from the time-course of $\langle I_W \rangle$ (Fig. 2a). The upwelling season occupied September 94 and from March to September 95 and the downwelling season, from October 94 to February 95. Although the surveyed dates are too spaced to follow the short-time evolution of the wind-featured events, all the expected contrasting hydrographic conditions characteristic of the study area were sampled. The response of the water column at stn 13 to alternative upwelling and relaxation conditions during the upwelling season can be appreciated in the peaks and thoughts of the ≤13°C isotherms (Fig. 2c), which trace the transgressions and regressions of oceanic ENACW in the shelf. Upwelling conditions were sampled during surveys 10 (Sept. 29) , 22 (Mar. 23), 27 (Jun. 8) and 31-32 (Aug. 3-24), coinciding with strong northerly winds (Fig. 2a). Conversely, upwelling relaxation occurred during surveys 9 (Sept. 8), 26 (May 25), and 29-30 (July 6-20), coinciding with wind calms. Water-column stability during upwelling relaxations was mainly due to thermal stratification, as continental runoff was very limited during the upwelling season (Doval et al., 1997a). On the contrary, the freshwater influence was relevant during the downwelling season (Fig. 2b), being maximum by October-November (survey 12-13). The most striking hydrographic event during the downwelling season was the presence of very warm (>16°C) and salty (>35.8 psu) water all over the water column by December (surveys 15 and 16). This water of subtropical origin was carried by the characteristic poleward slope current, developed in the NW Iberian upwelling system during the downwelling season (Frouin et al., 1990; Haynes and Barton, 1990; 1991). The downwelling front between the oceanic and continental-shelf waters moves all along the shelf as a function of the balance between river discharge, which tents to keep the front on the slope, and southerly-wind stress, which tents to displace the front towards the Rías Baixas (Álvarez-Salgado et al., 1996b). For a detailed description of the hydrographic and associated chemical conditions during the sampling period see Doval et al. (1997a).

3.2. *Organic matter distributions*

The average PON and POC profiles at the sampling site, stn 13 (Fig 3a-b): (**1**) displayed the expected maximum values at the surface, resembling the distribution of chl-*a* (not shown); (**2**) decreased to a minimum at 50 m, and (**3**) increased monotonically to the bottom, probably due to resuspension of organic rich sediments. Pelagic sediments off the Rías Baixas show an organic matter content usually >6 % (López-Jamar et al., 1992). This observation connects with the intense organic matter mineralization previously observed in shelf bottom waters from nutrient distributions (Fraga, 1981; Álvarez-Salgado et al., 1993; Prego and Bao, 1997; Álvarez-Salgado et al., 1997). The average profile of the C/N molar ratio (Fig. 3c) showed a significant increase with depth ($F_{6,127}$ = 7.25, p< 0.001), a commonly observed trend world-wide due to the more intense recycling of nitrogenous regarding carbonaceous compounds and the resuspension of C-rich POM (Copin-Montégut and Copin-Montégut, 1983). In spite of the C/N variability, the direct correlation of PON and POC for the whole data set at stn 13 (regression model II; Sokal and Rholf, 1995) was very high, r = +0.95 (Fig. 4a). The slope was 6.5±0.2 mol-C·mol-N^{-1}, the Redfieldian C/N molar ratio of phytoplankton biomass (Redfield et al., 1963). The outlayers in a circle corresponded to the previously observed C-rich POM resuspended form the sediments during the downwelling season.

Extreme DOC concentrations were recorded during the upwelling season: the highest values (>100 µM-C) in warm surface waters during prolonged upwelling relaxations and the lowest values (<70 µM-C) in recently upwelled cold bottom waters (Fig. 2e), paralleling the distribution of temperature (Fig. 2c). During the downwelling season, much lower surface DOC levels were recorded, accompanied by low temperatures and reduced chl-*a* levels. DOC and chl-*a* were not coupled in a daily time-scale (r^2 = 0.17). Chl-*a* accumulation in upwelling systems use to occur during the 'spin-down' phase of upwelling events, when nutrients are abundant and horizontal transport is reduced (Zimmerman et al., 1987; Álvarez-Salgado et al., 1996b; Doval et al., 1997b). Conversely, the subsequent DOC accumulation seems to take place after several days of wind relaxation, when phytoplankton growth is limited by nutrient availability. Although the sampling frequency did not allow us to monitor a complete cycle to test this hypothesis, large DOC accumulation is usually observed during the decline of phytoplankton blooms (Kirchman et al. 1994; Norrman et al., 1995; Chen et al., 1996).

Average DON and DOC (Fig. 3d-e) decreased monotonically with depth. The largest range of variation was observed in the upper layer, where the values ranged from the winter baseline to the highest concentrations during upwelling relaxations. The time-course of the DON and DOC profiles were also very similar, the direct correlation (regression model II; Fig. 4b) being higher (r = +0.79) than usually found in the literature (Jackson and Williams, 1985; DON subgroup report, 1993). The slope of the correlation (*i.e.* the average C/N ratio of DOM linked to the net production of nitrogen-containing biomolecules) was 12.0 ±0.7 mol-C·mol-N^{-1}, much higher than the average C/N ratio of the phytogenic organic material, as commonly observed world-wide (Jackson and Williams, 1985; Hansell et al., 1993; Williams, 1995; Chen et al., 1996; Hansell and Waterhouse, 1997). The origin intercept (13±4 µM), *i.e.* the fraction of DOC which does not covary with nitrogen, must be related to carbonaceous material. It represented ~18% of the average total DOC at stn 13, which is close to the percentage of total carbohydrate regarding DOC reported by Pakulski and Benner (1994) in surface ocean waters (21±7%). Although the average DOC/DON ratio was ~15 mol-C·mol-N^{-1} and did not change significantly with depth (Fig. 3f), the range of variation was very wide (from 11 to 18 mol-C·mol-N^{-1}) due to the weak coupling between the production of DON and DOC and the variable molecular composition of DOM (Jackson and Williams, 1985; Kirchman et al., 1991).

N-nutrients are exhausted in shelf surface layer off the Ría de Vigo during periods of wind relaxation (Doval et al., 1997a), *i.e.* when DOM accumulation occurs. Therefore, the observed excess of carbon-rich DOM can be due to reduced bacterial activity in N-nutrient depleted waters as suggested by Williams (1995) and Thingstad et al. (1997). Alternatively, the production of phytogenic C-rich DOM such as mono- and polysaccharides has also being suggested (Ittekkot et al., 1981; Kirchman et al., 1991; Benner et al., 1992; Pakulski and Benner, 1994; Norrman et al., 1995). It is interesting to note that the accumulation of DON when N-nutrients are depleted indicate that there must be a certain fraction of DON which is not easily degradable by bacteria or that bacterial activity can be limited by predation (Thingstad et al., 1997).

3.3. *Production of degradable DOM in the upper layer*

The DOC excess in the upper layer of stn 13 during the productive upwelling season can be roughly estimated using a simple 2-endmember mixing model. The average *T/S* diagram, considering all samples collected during the upwelling season (Fig. 5a), shows that the observed hydrographic structure can be approached by the direct mixing of recently upwelled ENACW from 50m to the bottom (salinity 35.72; temperature 12.5°C) and surface waters, *i.e* ENACW strongly modified by insolation and the influence of continental waters outwelled from the 'rías' (salinity 35.38; temperature 15.6°C). Considering that salinity behaved conservatively, the DOC concentration at 5, 20, 30 and 40m expected by simple mixing of the continental endmember (C) and the ENACW endmember can be estimated as ($DOC_{CONSERV}$):

$$DOC_{CONSERV} = \frac{S}{S_{ENACW}} \cdot DOC_{ENACW} + \frac{S_{ENACW} - S}{S_{ENACW}} \cdot DOC_{C}$$

where S is the average salinity at 5, 20, 30 or 40m; DOC_{ENACW} and S_{ENACW} are the average DOC and salinity from 50m to the bottom (67 µM-C and 35.72, respectively); and DOC_C is the DOC concentration in the continental discharge (~500 µM-C during the upwelling season; Doval et al., 1997b). Figure 5b showed the average $DOC_{CONSERV}$

profile at stn 13. The effect of the DOC-rich continental waters was only significant at the surface, where $DOC_{CONSERV}$ increased to 72 µM-C. The difference between the average DOC and $DOC_{CONSERV}$ profiles was the average DOC produced ($DOC_{PRODUCED}$) during the upwelling season. It is interesting to remark that $DOC_{PRODUCED}$ at 20, 30 and 40m did not result from dilution of the DOC-rich surface water ($DOC_{PRODUCED}$ = +26 µM-C) with upwelled ENACW ($DOC_{PRODUCED}$= 0 µM-C); it was clearly higher than expected from simple mixing (doted line in Fig. 5c). The same kind of calculation can be drawn for DON, but we only have 2 levels in the upper 50m. Average DON_{ENACW} and DON_{C} during the upwelling season were 4.6 and ~30 µM-N (Doval et al., 1997b), respectively. The calculated $DON_{PRODUCED}$ at 5 and 30m were +1.7 and +0.7 µM-N, respectively.

The DOC carried to stn 13 by recently upwelled ENACW during the upwelling season (67 µM-C) must be essentially allochthonous to the shelf and, to a large extend biologically inert. The minor allochthonous freshwater contribution to stn 13 (~5 µM-C at the surface) is expected to be also inert. On the contrary, the observed $DOC_{PRODUCED}$ in the upper 50m may be considered as a mix of a minor fraction of highly-labile DOC (recycling time, hours-days) and a major fraction of semi-labile DOC (recycling time, weeks-months) generated by biological processes (Kirchman et al., 1993, Carlson and Ducklow, 1995) Alternatively, Thingstad et al. (1997) have suggested accumulation of labile DOM caused by low growth rate of bacteria because of competition with phytoplankton for nutrients and/or low bacterial biomass because of predation. The average $DOC_{PRODUCED}$ at the surface was +26 µM-C (Fig. 5b), *i.e*. 27% of the average total concentration during the upwelling season (97 µM-C). The excess clearly decreased with depth to +15 µM-C at 20 m, +12 µM-C at 30 m and only +7 µM-C at 40

m. Comparing the average $DOC_{PRODUCED}$ with POC in surface waters, *i.e*. comparing the extend of the biologically usable organic carbon pools, it resulted that ~60% corresponded to $DOC_{PRODUCED}$. It contrasted with the 86% which is obtained when comparing the average total concentrations of DOC (97 µM-C) and POC (16.5 µM-C) in the surface. The same calculation for DON yielded that ~40% of the organic nitrogen produced in shelf surface waters was DON, while 73% was obtained from the direct comparison of the average total DON (6.7 µM-N) and PON (2.5 µM-N) concentrations during the upwelling season. Extending this calculation to the upper 50m, ~50% and ~35% of the organic carbon and nitrogen susceptible of biological utilisation was in the dissolved form, respectively. These calculations are conservative as DOC carried by the oceanic and freshwater endmembers have been considered inert. However, DOC in recently upwelled ENACW was ~10-20 µM-C higher than the refractory pool (recycling time, years) in deep waters of the NW Mediterranean (~50-58 µM-C; Copin-Montégut and Avril, 1993), the Equatorial Atlantic (46±7 µM-C; Thomas et al., 1995) or the NW Atlantic (~50-55 µM-C; Chen et al., 1996). DOC levels are even lower in the much older deep waters of the Pacific (~40 µM-C; Carlson and Ducklow, 1995; Peltzer and Hayward, 1996; Sharp et al., 1995). In addition, photochemical degradation of refractory DOC into labile compounds (Kieber et al, 1990; Mooper et al., 1991; Wetzel et al., 1995; Zhou and Mopper, 1997) could be an important issue in an upwelling system as the study area.

3.4. *Origin and fate of the DOM excess in shelf waters*

Comparison of the average levels of DOC during the upwelling season at the three stations surveyed (Fig. 6) will allow discussion on the relative importance of in situ production of DOC at stn 13 compared to the import from the Ría de Vigo and the export to the open ocean compared to the oxidation on the shelf.

Surface DOC clearly decreased ocean-wards: average DOC during the upwelling season was 106 µM-C at stn 15, 97 µM-C at stn 13 and only 79 µM-C at stn 11. The DOC excess in the surface layer compared to the mixing line (dotted line in Fig. 7a) between bottom ENACW at the outermost station (65 µM-C) and continental water (~500 µM-C), dramatically decreased from stn 15 to stn 11. Average DOC concentration in the surface layer of stn 15 during the upwelling season exceeded +32 µM-C the expected concentration by mixing (Fig. 7a). Considering a simple 2-D circulation model (Fig. 7b; Barber and Smith, 1981; Álvarez-Salgado et al., 1993), such an excess was produced during the long path of ENACW from the bottom of stn 11 to the surface of stn 15. According to Doval et al. (1997b), most of the DOC excess observed at stn 15 (+22 µM-C; ~70%) was produced within the volume between the river mouth and stn 15 (0.68 Km^3; Fig. 7b). So, this excess was produced during the time interval which the ingoing bottom water at stn 15 required to upwell, to mix with continental water, and to flow-out through the surface up to stn 15: ~5 days, average for the upwelling season (*i.e* the net production rate was 4.4 $\mu M\text{-}C\cdot d^{-1}$; Doval et al., 1997b). The remaining 30% was produced during the transit of bottom ENACW from stn 11 to the stn 15 (~35 Km). DOC produced at stn 13 (+28 µM) partly resulted from dilution of the DOC observed at stn 15 with upwelled source ENACW between stn 13 and 15. In fact, +15 µM-C (54%) resulted from dilution (dashed line in Fig. 7a), whereas the remaining +13 µM-C (46%) must have been produced in surface waters between stn 13 and 15 (*i.e*. in the outer ‘ría’; 2.60 Km^3). The estimated residence time of water in the outer ‘ría’ during the upwelling season must be ~10 days, as the volume of the outer ‘ría’ is four times the volume of the inner ‘ría’ whereas flows are about twice in the outer than in the inner Ría de Vigo (Prego, 1993). Consequently, the estimated net DOC production rate between stns 15 and 13 was ~1.3 µM-C·d^{-1}, about 1/4 than in the inner ‘ría’. Finally, the average DOC excess at stn 11 (+12 µM-C), resulted mainly from the simple dilution of the DOC observed at stn 13 with upwelled source ENACW between stn 13 and stn 11 (−·− line in Fig. 7a), since a no-significant production of only +2 µM-C was perceived. As expected, the same pattern was observed for DON (not shown).

Consequently, the Rías Baixas seem to be the main source of biologically usable or labile DOC to shelf surface waters off the western coast of Galicia. The Rías Baixas act as biogeochemical reactors where the largest amounts of organic matter (both dissolved and particulate) are produced (Prego, 1993; Álvarez-Salgado et al., 1996a). A considerable fraction of the particulate organic matter produced into the ‘rías’ did not reach the shelf because of preferential sedimentation and subsequent degradation within these embayments: following Prego (1993) the Ría de Vigo exports only 1/3 of the annual net community production. On the contrary, the labile DOM produced into the ‘rías’ is preferentially outwelled to the shelf: Álvarez-Salgado et al (1996a) suggested that 2/3 of the outgoing organic matter from the Ría de Arousa should be labile DOM to equal the balance between nutrient consumption and organic matter production.

The probable fate of this labile dissolved organic material produced into the ‘rías’ is the simple dilution with upwelled DOM-poor ENACW and the export to the open-ocean surface waters, as observed between stations 13 and 11. Recurrent filaments off the ‘rías’ during the upwelling season must clearly enhance the shelf edge-exchange, favouring export *versus* oxidation on the shelf. Filaments start by May, takes their largest size by September, and ceases by October (Haynes et al., 1993). The filament just south of the Rías Baixas is among the longest of all the observed off the Iberian Peninsula (Haynes et al., 1993). Once in the open ocean, we could speculate that seasonally accumulated DOM should be transported northward by the warm and salty poleward flow on the slope, characteristic of the downwelling season (Haynes and Barton, 1990; 1991). Finally, at the time of the deep winter mixing (by February-March; Fraga et al., 1982), massive downward transport of the accumulated DOM should occur in the open ocean, which would contribute to dissolved oxygen consumption in subsurface waters, playing a major role in the new production of the system (Carlson et al., 1994; Bronk et al., 1994; Lefèvre et al., 1996).

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Figure captions

Fig. 1. Map of the study area showing the position of the sampling sites (stn 11, 13 and 15) and the centre of the cell to calculated geostrophic winds (stn G1). The 100 and 200 m isobaths are also included.

Fig. 2. Time course of **a**) $<I_W>$ at stn G1, in 10^{-3} $m^3 \cdot s^{-1} \cdot km^{-1}$; **b**) CTD-salinity; **c**) CTD-temperature, in °C; **d**) particulate organic carbon (POC), in µM-C; and **e**) dissolved organic carbon (DOC), in µM-C at stn 13 from September 1994 to September 1995.

Fig. 3. Box and Whisker plot of **a**) particulate organic nitrogen (PON), in µM-N; **b**) particulate organic carbon (POC), in µM-C; **c**) POC/PON, in mol-C·mol-N^{-1}; **d**) dissolved organic nitrogen (DON), in µM-N; **e**) dissolved organic carbon (DOC), in µM-C; and **f**) DOC/DON, in mol-C·mol-N^{-1} for the whole data set at stn 13. Fifty percent of the data are included within the limit of the boxes and the caps represents the 10th and 90th percentiles. Solid lines represent the average profiles. Although DON samples were collected at all depths, analyses were performed only at 5, 30, 50 and 85m.

Fig. 4. X-Y plot of **a**) PON-POC and **b**) DON-DOC for the whole data set at stn 13. Solid lines represent the corresponding regression lines (Model II; Sokal and Rolhf, 1995). Concentrations in µM

Fig. 5. Degradable DOC produced during the upwelling season at stn 13. **a**) average T-S diagram; **b**) average DOC profile expected by simple mixing of the oceanic and freshwater endmembers (open circles) and average actual DOC profile (solid circles); and **c**) average calculated DOC excess versus salinity.

Fig. 6. Box and Whisker plot of dissolved organic carbon (DOC) during the upwelling season at **a**) stn 15; **b**) stn 13; and **c**) stn 11. Fifty percent of the data are included within the limit of the boxes and the caps represents the 10th and 90th percentiles. Solid lines represent the average profiles. Concentrations in µM-C.

Fig. 7. Degradable DOC excess at the surface of stn 15, 13 and 11 during the upwelling season (**a**) and schematic diagram of the characteristic 2-D circulation and mixing pattern in shelf waters of the NW Iberian upwelling system (**b**). (····) DOC-S mixing line between the oceanic (ENACW) and freshwater endmembers; (– – –) DOC-S mixing line between ENACW and surface water at stn 15; (–·–·–) DOC-S mixing line between ENACW and surface water at stn 13. Concentrations in µM-C.

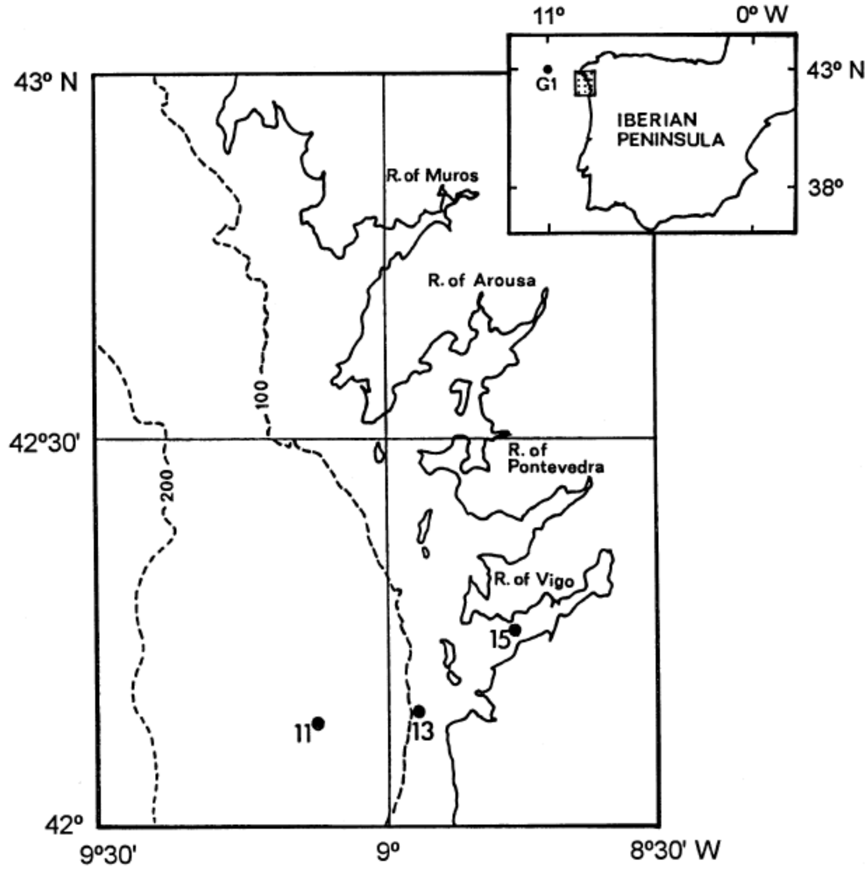
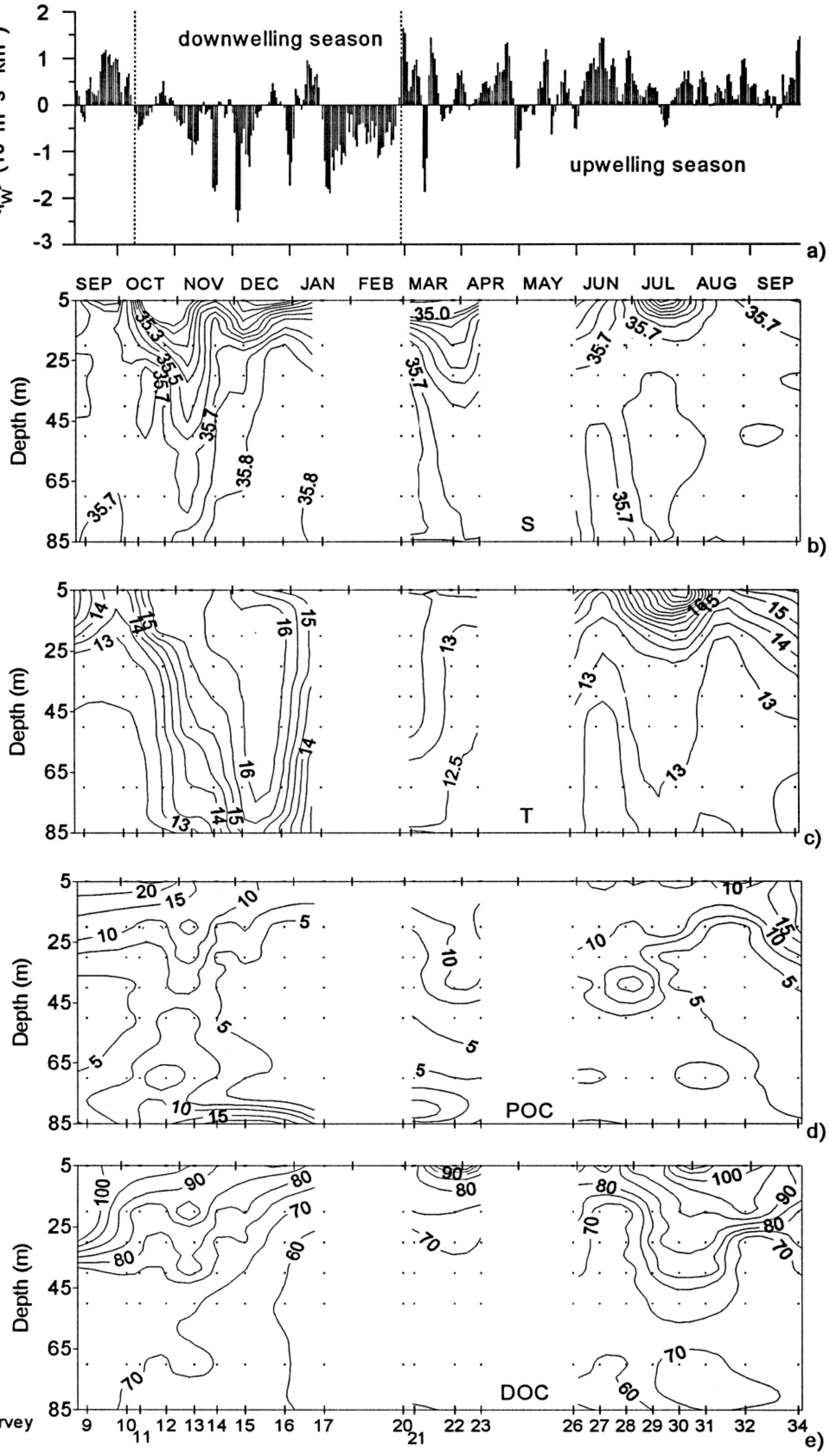

11°
0° W
43° N
G1
IBERIAN
PENINSULA
38°
43° N
R. of Muros
R. of Arousa
100
42°30'
200
R. of
Pontevedra
R. of Vigo
15
11
13
42°
9°30'
9°
8°30' W

Figure 1



downwelling season
upwelling season
<I_W> (10^3 m^3·s^{-1}·km^{-1})
a)
SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP
Depth (m)
S
b)
T
c)
POC
d)
DOC
e)
survey
9 10 11 12 13 14 15 16 17 20 21 22 23 26 27 28 29 30 31 32 34

Figure 2

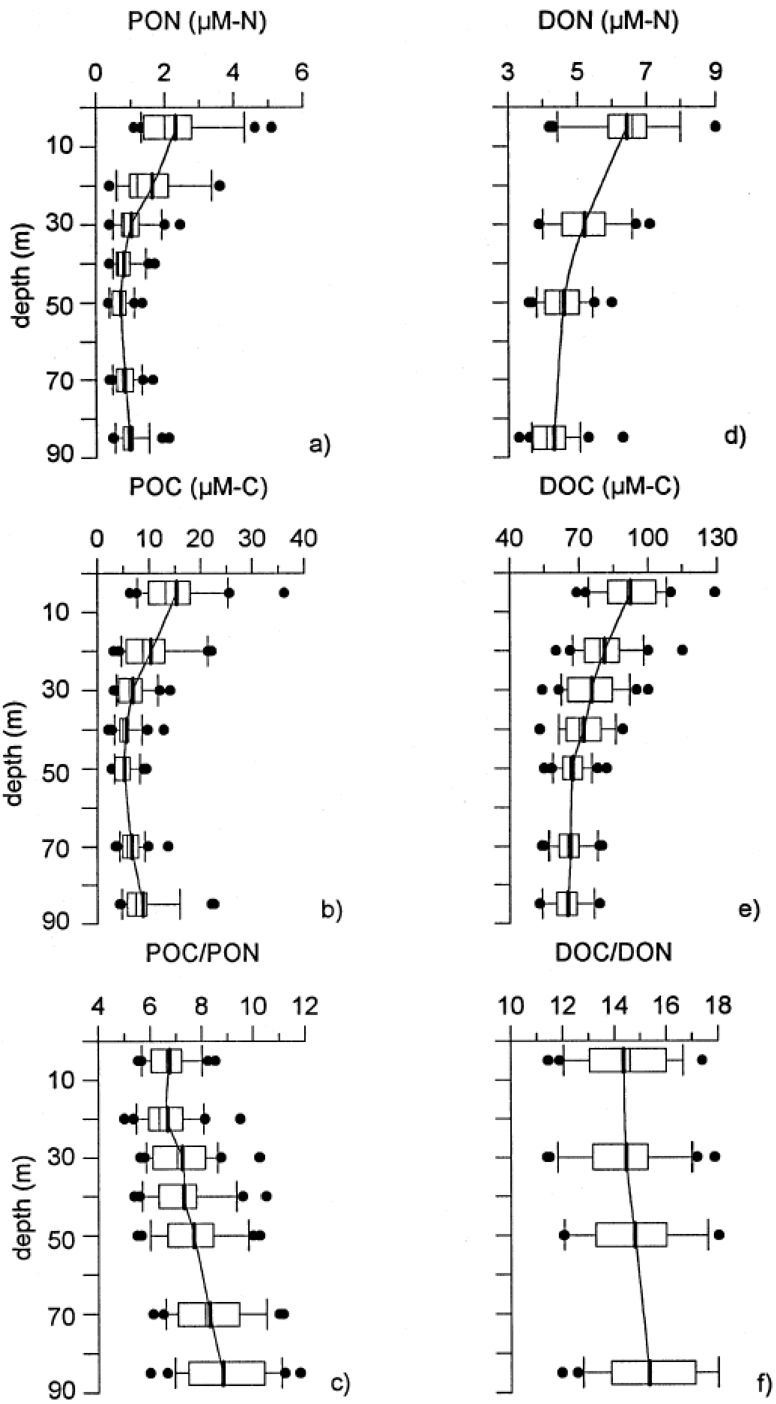
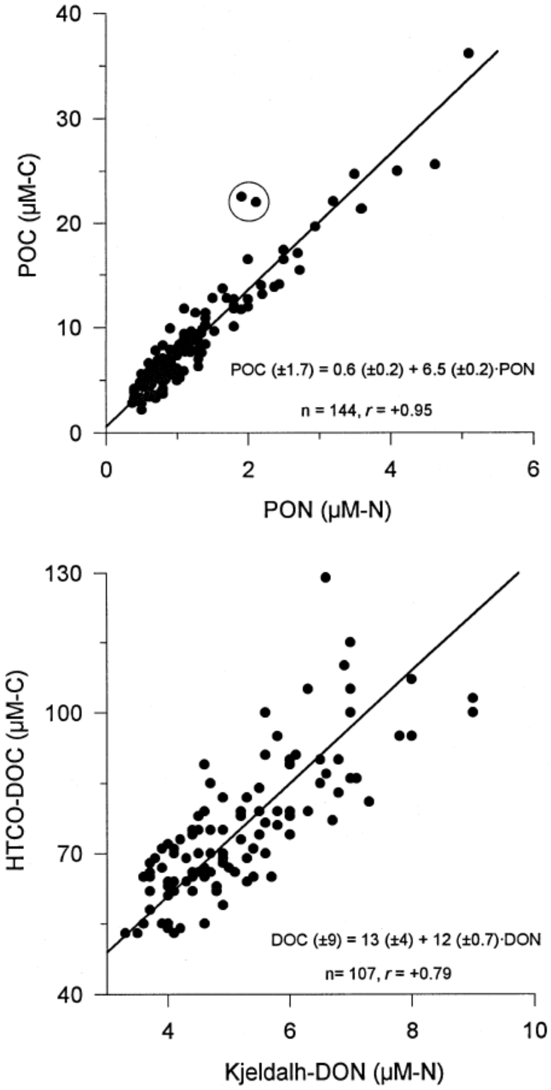

PON (µM-N)
0 2 4 6
DON (µM-N)
3 5 7 9
POC (µM-C)
0 10 20 30 40
DOC (µM-C)
40 70 100 130
POC/PON
4 6 8 10 12
DOC/DON
10 12 14 16 18
depth (m)
10 30 50 70 90
a)
b)
c)
d)
e)
f)

Figure 3



POC (μM-C)
PON (μM-N)
POC (±1.7) = 0.6 (±0.2) + 6.5 (±0.2)·PON
n = 144, r = +0.95
HTCO-DOC (μM-C)
Kjeldalh-DON (μM-N)
DOC (±9) = 13 (±4) + 12 (±0.7)·DON
n= 107, r = +0.79

Figure 4

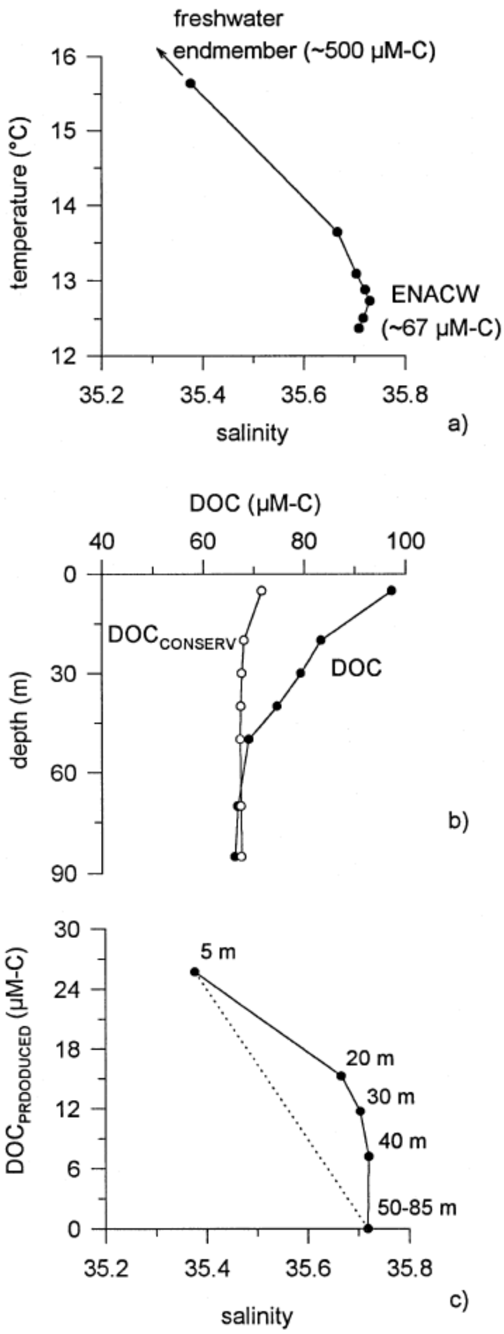

freshwater
endmember (~500 µM-C)
temperature (°C)
ENACW
(~67 µM-C)
salinity
a)
DOC (µM-C)
depth (m)
DOC
CONSERV
DOC
b)
DOC
PRODUCED
(µM-C)
5 m
20 m
30 m
40 m
50-85 m
salinity
c)

Figure 5

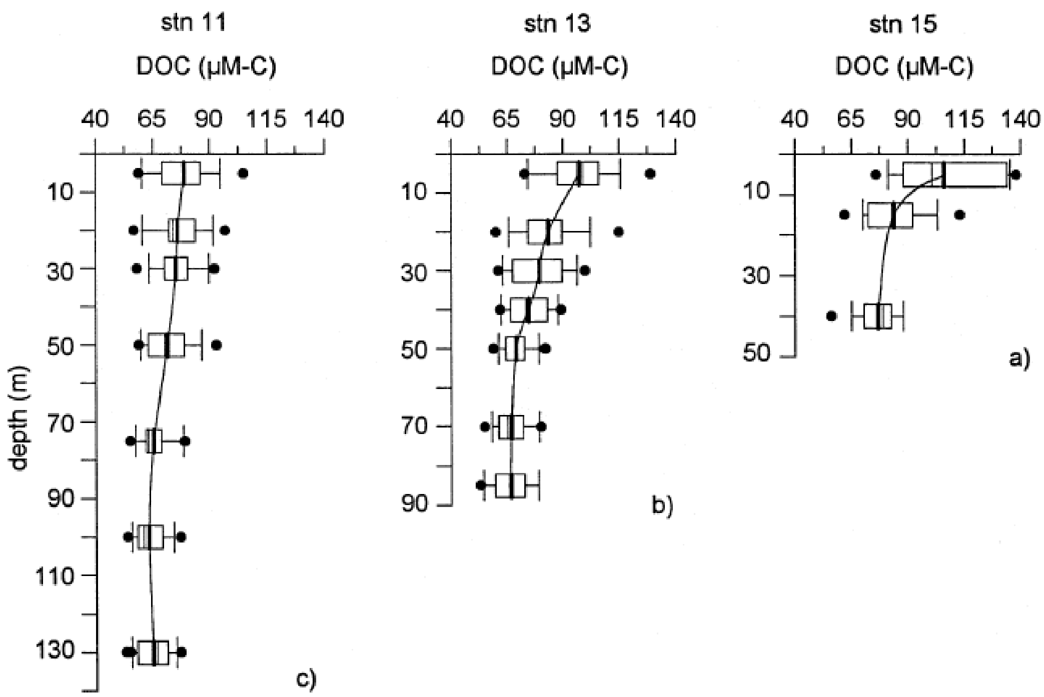
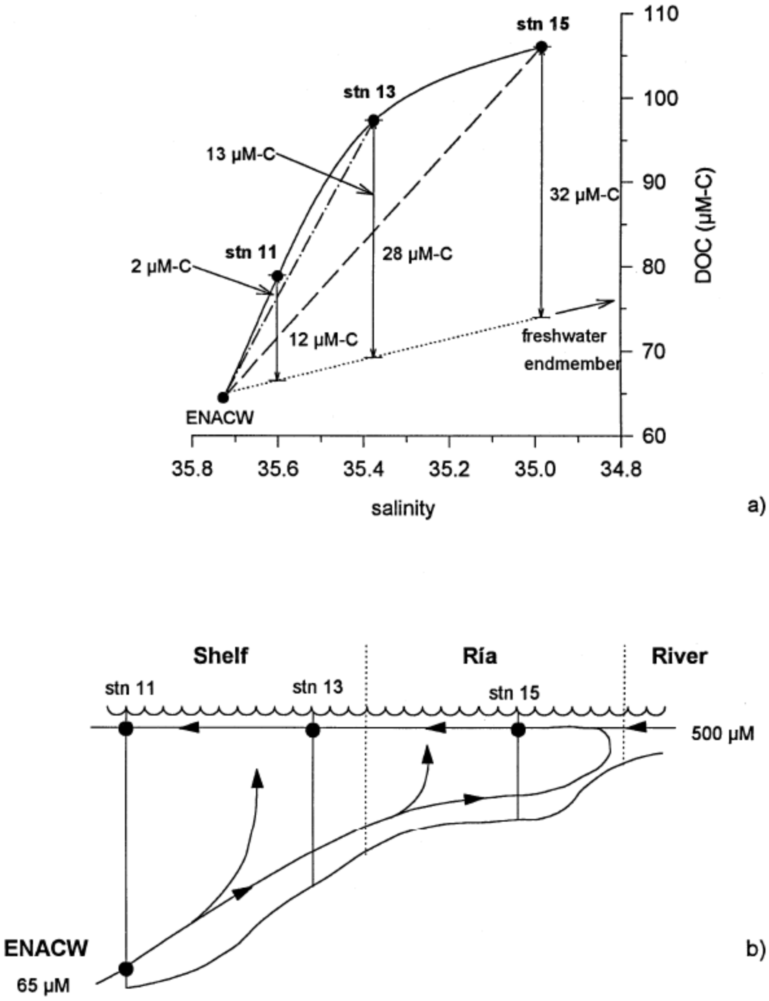

stn 11
DOC (µM-C)
40 65 90 115 140
depth (m)
10
30
50
70
90
110
130
c)
stn 13
DOC (µM-C)
40 65 90 115 140
10
30
50
70
90
b)
stn 15
DOC (µM-C)
40 65 90 115 140
10
30
50
a)

Figure 6



stn 15
stn 13
13 µM-C
32 µM-C
stn 11
2 µM-C
28 µM-C
12 µM-C
freshwater
endmember
ENACW
110
100
90
80
70
60
DOC (µM-C)
35.8
35.6
35.4
35.2
35.0
34.8
salinity
a)
Shelf
Ría
River
stn 11
stn 13
stn 15
500 µM
ENACW
65 µM
b)

Figure 7